An Examination of Historical Lake and Stream Chemistry in North Central Ontario- Can Case Histories Document Acidification?

J.E. Gray and J.R.M. Kelso

Great Lakes Fisheries Research Branch,
1219 Queen Street East,
Sault Ste. Marie,
Ontario
P6A 5M7

May, 1984.

Canadian Technical Report of Fisheries and Aquatic Sciences No. 1223

Canadian Technical Report of Hydrography and Ocean Sciences

Technical reports contain scientific and technical information that contributes to existing knowledge but which is not normally appropriate for primary literature. The subject matter is related generally to programs and interests of the Ocean Science and Surveys (OSS) sector of the Department of Fisheries and Oceans.

Technical reports may be cited as full publications. The correct citation appears above the abstract of each report. Each report is abstracted in *Aquatic Sciences and Fisheries Abstracts* and indexed in the Department's annual index to scientific and technical publications.

Technical reports are produced regionally but are numbered nationally. Requests for individual reports will be filled by the issuing establishment listed on the front cover and title page. Out of stock reports will be supplied for a fee by commercial agents.

Regional and headquarters establishments of Ocean Science and Surveys ceased publication of their various report series as of December 1981. A complete listing of these publications is published in the *Canadian Journal of Fisheries and Aquatic Sciences*, Volume 39: Index to Publications 1982. The current series, which begins with report number 1, was initiated in January 1982.

Rapport technique canadien sur l'hydrographie et les sciences océaniques

Les rapports techniques contiennent des renseignements scientifiques et techniques qui constituent une contribution aux connaissances actuelles, mais qui ne sont pas normalement appropriés pour la publication dans un journal scientifique. Le sujet est généralement lié aux programmes et intérêts du service des Sciences et leves océaniques (SLO) du ministère des Pêches et des Océans.

Les rapports techniques peuvent être cités comme des publications complètes. Le titre exact paraît au-dessus du résumé de chaque rapport. Les rapports techniques sont résumés dans la revue *Résumés des sciences aquatiques et halieutiques*, et ils sont classés dans l'index annuel des publications scientifiques et techniques du Ministère.

Les rapports techniques sont produits à l'échelon régional, mais numérotés à l'échelon national. Les demandes de rapports seront satisfaites par l'établissement auteur dont le nom figure sur la couverture et la page du titre. Les rapports épuisés seront fournis contre rétribution par des agents commerciaux.

Les établissements des Sciences et levés océaniques dans les régions et à l'administration centrale ont cessé de publier leurs diverses séries de rapports en décembre 1981. Une liste complète de ces publications figure dans le volume 39, Index des publications 1982 du *Journal canadien des sciences halieutiques et aquatiques*. La série actuelle a commencé avec la publication du rapport numéro 1 en janvier 1982.

Canadian Technical Report of

Fisheries and Aquatic Sciences 1223

May 1984

AN EXAMINATION OF HISTORICAL LAKE AND STREAM CHEMISTRY IN NORTH-CENTRAL ONTARIO - CAN CASE HISTORIES DOCUMENT ACIDIFICATION?

by

J. E. Gray and J. R. M. Kelso

Great Lakes Fisheries Research Branch
Department of Fisheries and Oceans
1219 Queen Street East
Sault Ste. Marie
Ontario
P6A 5M7

(c) Minister of Supply and Services Canada 1984
Cat. No. Fs 97-6/1223 ISSN 0706-6457

Correct citation for this publication:

Gray, J.E., and J.R.M. Kelso. 1984. An examination of historical lake and stream chemistry in north-central Ontario - can case histories document acidification? Can. Tech. Rep. Fish. Aquat. Sci. 1223: v + 38 pp.

ABSTRACT

Gray, J.E., and J.R.M. Kelso. 1984. An examination of historical lake and stream chemistry in north-central Ontario - can case histories document acidification? Can. Tech. Rep. Fish. Aquat. Sci. 1223: v + 38 pp.

Historical chemistry data for lakes in the Sault Ste. Marie and Blind River Ministry of Natural Resources administrative districts of Ontario and streams draining the Canadian Shield into Lake Huron and Lake Superior were amassed regardless of source. Data were available for 117 lakes and 33 streams. No statistically significant changes occurred for H^+, alkalinity, or conductivity in lakes. In streams, a significant decrease over time in alkalinity and conductivity was found for data collected in the spring. Where good cation and anion data were available, greatest decreases from expected alkalinities occurred in areas of highest deposition. Constraints imposed by differing sampling and analytical methodologies hampered an overall definitive analysis of chemical change through time although a substantial data base is available. It is our conclusion that some data sets may foster construction of reliable individual lake/stream case histories but a province-wide approach using all available data would be questionable. An alternative to assessing historical rate of change in lakes or streams is to implement an appropriate continuing monitoring program.

RESUME

Gray, J.E., and J.R.M. Kelso. 1984. An examination of historical lake and stream chemistry in north-central Ontario - can case histories document acidification? Can. Tech. Rep. Fish. Aquat. Sci. 1223: v + 38 pp.

RÉSUMÉ

On a recueilli, sans tenir compte de leur source, des données disponibles sur la chimie des lacs des districts administratifs du ministère ontarien des ressources naturelles, de Sault-Sainte-Marie et de Blind River, et sur la chimie des cours d'eau drainant le Bouchlier canadien et se jetant dans le lac Huron et le lac Supérieur. Il existait des données pour 117 lacs et 33 cours d'eau. Les lacs ne présentaient aucune modification statistiquement significative de la concentration en ions H^+, de l'alcalinité ou de la conductivité. Les cours d'eau présentaient une diminution significative de l'alcalinité et de la conductivité avec le temps, pour les données recueillies au printemps. Lorsqu'il existait de bonnes données sur la concentration anionique et cationique, on a constaté les plus grandes diminutions de l'alcalinité prévue dans les régions où le dépôt était le plus important. Vu les contraintes imposées par

l'emploi de différentes méthodes d'échantillonnage et d'analyse, il a été impossible de faire une étude définitive globale des modifications chimiques avec le temps, même si l'on disposait d'une importante base de données. En conclusion, certaines séries de données peuvent favoriser l'élaboration de dossiers individuels fiables sur les lacs et les cours d'eau, mais une approche à l'échelle provinciale qui reposerait sur toutes les données disponibles serait douteuse. La mise en oeuvre d'un programme permanent de contrôle approprié permettrait aussi d'évaluer le taux de modification des lacs et des cours d'eau.

INTRODUCTION

Documentation of the acidification of lakes and streams in Canada using historical data has shown significant decreases in either pH or alkalinity for 16 lakes in Halifax County, Nova Scotia (Watt et al., 1979), the La Cloche Mountain lakes in the Killarney, Ontario area (Beamish & Harvey, 1972), Clear Lake in Haliburton County, Ontario (Dillon et al., 1978), and for numerous rivers in Nova Scotia (Thompson et al., 1980). General uncertainty, however, over the impact of long range transport of atmospheric contaminants on remote inland lakes and streams over time still remains, since only a few case histories are available. It was important, then, that the analysis of two of Ontario's unique historical limnological records, the Ontario Ministry of Natural Resources (OMNR) lake inventory data, and the Ontario Ministry of the Environment (OME) stream water quality data (along with any other sources) be examined to identify any historical trends.

BACKGROUND TO THE STUDY

The OMNR districts of Sault Ste. Marie and Blind River were chosen as 'test grounds' for the examination of historical lake chemistry (Fig. 1). This chemical data originated from lake surveys

initiated by the OMNR approximately 14 years ago to obtain initial information on the fisheries of inland lakes. As well as identifying fish species and age class structure of any sports fish population, lake survey crews defined lake morphometry, and measured oxygen, pH, alkalinity, and conductivity. While many lakes have since been resurveyed, there has been no analysis of these multiple observations for chemical trends over time.

Combined land area of the two districts is 13,254 km^2 with inland lakes covering 11 percent (1,409 km^2) (Armscrong & Simpson, 1982). Although this lake surface area is only one percent of the provincial inland lake total, the water to land ratio is above average for the province but typical of the Canadian Shield (Williams, 1982).

Historical chemistry from streams located between Thunder Bay on Lake Superior and Parry Sound on Georgian Bay was obtained from several sources (Table 1). The earliest recorded chemistry resulted from measurements to determine the strength of lampricide treatments to lamprey spawning streams by the Sea Lamprey Control Centre (Department of Fisheries and Oceans) in Sault Ste. Marie. The longest chemical record was obtained from the OME. Data was also obtained from a regional OME episodic sampling program undertaken between 1979 and 1981 (OME, Northeastern Region, unpublished data; Keller & Gale, 1982). Recent water quality data were obtained by the staff of the

Great Lakes Fisheries Research Branch (Department of Fisheries and Oceans) at Sault Ste. Marie and at Owen Sound, who have been monitoring episodic chemical conditions in streams since 1979 (Table 1).

The majority of the watersheds of the lakes and streams are located in areas underlain with early Precambrian granitic and meta-volcanic bedrock assemblages covered with predominantly acid Podzolic soils (Lucas & Cowell, 1982). These terrain characteristics indicate that the districts have low buffering capacity and hence surface waters are sensitive to acidification from atmospheric deposition (Figs. 1 and 2).

Little detailed information on deposition is available. However, the mean annual pH of precipitation in the Sault Ste. Marie district ranged from a high of 4.52 in 1976 to a low of 4.25 in 1979 (Kelso et al., 1982). Snow samples in 1981 were consistently acidic with a mean pH of 4.7 ± SD 0.44 (n = 58) during the months of March and April and a mean pH of 4.3 (n = 12) during March before snowmelt began (Kelso, unpublished data). The area between Parry Sound and north of Sault Ste. Marie is impacted by at least twice the airborne SO_4^{2-} (Barrie & Sirois, 1982) as the area from just north of Sault Ste. Marie to Thunder Bay (Fig. 1).

The Parry Sound area received more precipitation during April (normal 71 mm), September (normal 111 mm), and annually (1094 mm) than Sault Ste. Marie (April normal 64 mm, September normal 95 mm, annual normal 898 mm), or Thundery Bay (April normal 47 mm, September normal 89 mm, annual normal 723 mm). The Thunder Bay area received considerably less snowfall (24 percent of annual precipitation) than either Sault Ste. Marie (30.4 percent) or Parry Sound (30 percent) (Can. Atmos. Environm. Serv., 1982).

Two approaches to data treatment were used. First, historical records of stream and lake water pH, alkalinity, and conductivity were examined over time to identify significant changes. Second, recent measurements of alkalinity, Ca^{++}, Mg^{++}, and SO_4^{2-} were used to determine if shifts in expected ion balances were evident.

SAMPLING AND ANALYTICAL PROCEDURES

A major concern regarding historical data is the degree of error associated with inconsistent analytical and sampling methods. The first problem was how accurately a single sample would represent the water quality of a lake or stream where chemistry could fluctuate hourly, daily, and seasonally. If one assumes that daily and seasonal fluctuations are random and normally distributed and if all chemistry

was taken during the day and during the same season, a valid assessment of trends may result.

Two or more years of pH, alkalinity, and conductivity data were available for 64 lakes in the Sault Ste. Marie district and 53 lakes in the Blind River district (total of 117 lakes). For 32 streams, an average of 6.4 ± SD 2.2 years of spring data and 8.1 ± SD 3.8 years of fall data were analyzed.

Stream chemistry was divided between spring and fall. April was chosen as the most likely time to observe snow melt chemical fluxes with September having less discharge-related influence (Fig. 3). An examination of streamflow data suggested that chemistry may not have always been collected during the peak of spring runoff. The yearly variation in streamflow, however, was slight during the month of April. Surveyed streams draining into Lake Superior and the North Channel of Lake Huron had mean annual discharges ranging from 2 m^3 sec^{-1} to 368 m^3 sec^{-1} (mean 68 m^3 sec^{-1}) and watersheds ranging in size from 108 km^2 to 2455 km^2 (mean 1108 km^2 ± SD 765 km^2). Streams draining into Georgian Bay had smaller watershed areas, mean 478 km^2 ± SD 362 km^2, and less mean annual discharge, mean 57 m^3 sec^{-1} (Fig. 3).

Lake chemical data were confined to the summer months of June, July, and August. Most lake samples were taken at the surface from 1960 to 1970, at discrete depths during the 1970's and in recent years a 'tube' composite of the water column from the lake surface to the bottom of the metalimnion was used (Table 2). Chemical variables were averaged from discrete depth samples (referred to as integrated samples). An average of only 2.5 years of data per lake was obtained which necessitated the comparison of chemistry obtained by any sampling method; however, all samples were from the water column above the bottom of the metalimnion. Stream samples were 'grab' samples taken from just below the water surface (Ontario Ministry of the Environment, 1981).

The second problem, and clearly the most difficult to overcome, was the difference in analytical methodologies through time. Before 1980, OMNR lake pH and alkalinity measurements were obtained colorimetrically. The Hellige pH gelatine colour discs were accurate only to 0.5 pH unit and generally overestimated the parameter (Goodchild, 1982). Debate over the interpretation of early colorimetric and later potentiometric pH measurements (Howells, 1982; Haines, 1982), would suggest that there may be no appropriate means to correct for methodology. If historical measurements overestimated pH and a decline in acidity had occurred, a cautious interpretation of

the magnitude of change would be required. The first step in this analysis, however, was to determine if a change had occurred.

OME data prior to 1975 were based on potentiometric pH measurements and total fixed endpoint (TFE) alkalinity titrations (Table 1). 1980 and 1981 pH data from all agencies were potentiometric measurements and alkalinity was determined using the 'total inflection point' (TIP) analytical methodology (Gran analysis) (Table 1). Although TFE alkalinity values may overestimate the 'true' value (TIP), particularly at low concentrations, there appears to be little agreement on the mathematical correction that can be made as TFE and TIP values do not have a constant linear relationship (Jeffries & Zimmerman, 1980; Kramer & Tessier, 1981; Burns et al., 1981). Alkalinity correction factors applied to our data did not change the trend through time results reported herein.

Low concentrations of sulphate before 1973 are questionable due to unreliable (Rawlings, 1982) laboratory techniques (Table 1). There is the added problem in the case of stream data, that comparisons were made between chemistries analyzed by four different agencies.

RESULTS AND DISCUSSIONS

The mean annual change in hydrogen-ion, alkalinity, and conductivity for each lake and stream was calculated by averaging the change in concentration per year over the entire time period. The null hypothesis (no change) was then tested using the t-test.

There was no bias with regard to the span of years between sampling periods, with a mean of 7.2 ± SD 3.7 years between lake pH and alkalinity readings, and 3.6 ± SD 2.0 years between lake conductivity measurements. Fall and spring measurements of stream pH were averaged over a period of 8.6 ± SD 4.3 years, alkalinity values of 7.0 ± SD 2.8 years, and conductivity values over 9.1 ± SD 4.0 years.

LAKES

Lake areas ranged from 0.1 to 27.1 km^2 (mean 2.3 km^2 ± SD 4.4 km^2), watershed areas from 0.6 to 641.4 km^2 (mean 29.2 km^2 ± SD 82.4 km^2), mean depths from 1.8 to 38.7 m (mean 9.8 m ± SD 7.0 m), and lake orders (the position of a lake within a drainage network (OMNR, 1980)) from 1 to 4 (mean 2.1 ± SD 1.0). Sixty-five percent (n = 75) of the lake watershed had low to insignificant buffering capacity and 26 percent (n = 41) had mixed geological

substrates resulting in low to high buffering throughout a watershed (after Shilts, 1981).

Alkalinity ($CaCO_3$) measured in 85 lakes ranged from 6.0 $\mu eq\ l^{-1}$ to 650 $\mu eq\ l^{-1}$ (mean 161.2 $\mu eq\ l^{-1}$ ± SD 127 $\mu eq\ l^{-1}$), conductivities in 60 lakes ranged from 20 $\mu mhos\ cm^{-1}$ to 185 $\mu mhos\ cm^{-1}$ (mean 47.32 $\mu mhos\ cm^{-1}$ ± SD 31.32 $\mu mhos\ cm^{-1}$), and pH ranged from 5.4 to 8.1 for 117 lakes (mean pH 6.9 ± SD 0.44). These measurements suggest that the lakes range from being very sensitive to not sensitive to acidic precipitation (after Minns, 1981).

Figure 4 summarizes the annual changes in three parameters from 117 lakes. The overall mean annual change in H^+ of -0.22×10^{-7} ± SD 1.15×10^{-7} mol l^{-1}, representing an increase in pH, was not significant ($t = 0.26$, $P < 0.05$). A mean annual increase in alkalinity as $CaCO_3$ of −14.15 ± SD 27.81 $\mu eq\ l^{-1}$ for 85 lakes was not significant ($t = 1.47$). Conductivity measurements for 60 lakes showed an insignificant mean annual increase of 0.4 ± SD 3.2m $\mu mhos\ cm^{-1}$ at 25°C ($t = 0.26$). Data analyzed for only order 1 lakes also showed no significant changes, with a mean annual decline in H^+ of -0.34×10^{-7} ± SD 1.59×10^{-7} mol l^{-1} in 34 lakes representing an increase in pH, an annual decline in alkalinity as $CaCO_3$ of −8.36 ± SD 40.7 $\mu eq\ l^{-1}$ in 21 lakes, and in 14 lakes with comparative conductivities an annual decline of −1.7 ± SD 2.3 $\mu mhos\ cm^{-1}$ at 25°C.

Relationships between the mean annual changes in the chemical parameters and the morphological and geological factors were weak (Table 3), with significant correlations occurring only between alkalinity, conductivity, and lake location. A breakdown of these morphometric variables between lakes with increasing and decreasing trends in the chemical parameters, as indicated in Table 4, would suggest that inconsistencies in the data or inadequate sample sizes should not be ruled out as confounding factors in the analysis of trends through time.

Figure 5 suggests that the minor (statistically insignificant) increases and decreases in annual measurements may be a result of sampling and analytical differences. Eighty-six percent of the first alkalinity values from 1960 to 1975 were TFE measurements. When compared with TIP measurements taken over the past several years annual changes of greater magnitude are apparent (Fig. 5). Since analytical techniques for pH were more consistent over time, the plot of annual changes in H^+ concentrations (Fig. 5) suggests that sampling techniques may influence the perceived magnitude of change through time. Changes from 1960 to 1970 are minimal and most comparisons were made between surface samples. From 1970 to the late 1970's comparisons were generally made between surface and integrated samples or between integrated samples. Changes observed over the past several years were comparisons between integrated and 'tube' composites or

between tube samples and the magnitude of the change is not as great as in previous years. The high number of observations in 1980 and 1981 result from an extensive OMNR Acid Precipitation in Ontario lake survey program.

The uncertainties of measurement techniques and the lack of statistical significance for any annual change may not rule out that some decrease in alkalinity, as evident in Fig. 6, has not occurred. Watersheds may have been influenced by atmospheric inputs of acids, responding with some decline in lake alkalinity, with little or no decrease in measured pH. If surveys had included measurements of cations and anions, acidification models (Henriksen, 1979, 1980, 1982) could have provided further insight.

STREAMS

Annual changes in H^+, alkalinity, and conductivity during the fall (33 streams) and spring (32 streams) are documented (Fig. 7). H^+ levels increased only slightly, $0.01 \times 10^{-7} \pm$ SD 0.09×10^{-7} mol l^{-1} ($t = 0.65$) in the fall, and $0.30 \times 10^{-7} \pm$ SD 4.44×10^{-7} mol l^{-1} ($t = 0.38$) in the spring (represents decreases in pH). A mean annual decrease of -24.6 μeq $l^{-1} \pm$ SD 183.5 μeq l^{-1} $CaCO_3$ (alkalinity) was not significant ($t = 0.76$) in the fall but an annual

spring decline of 27.9 $\mu eq\ l^{-1}$ ± SD 43.1 $\mu eq\ l^{-1}$ $CaCO_3$ was significant ($t = -3.66$) (measurements over 6.6 years ± SD 2.3 years). However, when changes in each individual stream's alkalinity were tested over time (t-test - mean annual change = 0) only the French River exhibited a significant ($P < 0.05$) annual change (increase of 13.4 $\mu eq\ l^{-1}$ $CaCO_3$ over 6 years). This change may be a result of changing land practices within the watershed, or faulty historical data. Fall conductivity measurements had a mean annual decrease of -1.4 $\mu mhos\ cm^{-1}$ ± SD 17.1 $\mu mhos\ cm^{-1}$, which was not significant ($t = 0.48$) (mean 7.3 measurements ± SD 3.3 measurements of 11.4 years ± SD 5.3 years). An annual decrease of -2.2 $\mu mhos\ cm^{-1}$ ± SD 4.0 $\mu mhos\ cm^{-1}$ in the spring data, however, was significant ($t = -3.21$) for the population of 32 streams (mean 5.5 measurement ± 1.5 measurements over mean 6.9 years ± SD 2.8 years). In contrast, changes in spring conductivity over time for individual streams were not significant.

In our poorly to moderately buffered systems, the cations Ca^{++} and Mg^{++}, and anions HCO_3^- and SO_4^{2-} were the overall dominant ions. The balance among these four ions persisted over the range of alkalinities.

In areas that may have experienced only slight acidification, strong acids from precipitation dominate the weathering process, releasing base cations into solution without bicarbonate

alkalinity being formed (Burns et al., 1981). The cation/HCO_3^- ratio may range from zero when acids from precipitation are the domninant source of H^+, to one when the main source of H^+ is the dissociation of CO_2 in water.

Figure 8 includes 1979 to 1981 data from streams with historical chemical records as well as data from streams with only one year of chemistry. The bicarbonate to Σ calcium and magnesium ratio was 0.46 (n = 6) for the low fall alkalinity (<200 μeq l^{-1} HCO_3^-) streams. The spring low alkalinity group had a ratio of 0.33 (n = 20). For the high alkaliuity group (>200 μeq l^{-1} HCO_3^- to Σ Ca^{++} + Mg^{++} ratio was 0.68 (n = 15) in the fall and 0.73 in the spring. These ratios are similar to those reported by Burns et al. (1981) for primarily small streams in the White Mountains of New Hampshire and lakes in Maine where acid precipitation has been shown to have lowered the pH and alkalinity of these waterbodies. Many surface waters in Scandinavia, the La Cloche Mountains, Ontario and Hubbard Brook, New Hampshire have bicarbonate to base cation ratios below 0.20 (Burns et al., 1981). Both the low and high alkalinity streams reflect the acid contribution from the Ontario snow pack in the spring.

Historical and recent HCO_3^-/cation ratios were compared for ten streams with fall data and 17 streams with spring data. Over the

past four years a mean annual spring decline of 0.02 in the ratio ($t = -0.35$) and an annual fall decline of -0.03 in the ratio over 13 years was not significant ($t = -0.35$).

The correlation between SO_4^{2-} and ($Ca^{++} + Mg^{++} - HCO_3^-$) for 21 streams with recent fall data is plotted in Fig. 9, and highlights the sensitivity of a number of streams showing evidence of an excess of sulphate.

The spatial distribution of streams in the low alkalinity group and low HCO_3^-/cation ratio group versus the high alkalinity and high HCO_3^-/cation ratio group generally correspond to three distinct regions of acidic atmospheric loading (Fig. 2). Low bicarbonate alkalinity systems and low spring HCO_3^-/cation ratios are observed in the broad regions of higher acidic atmospherc loading.

CONCLUSIONS

Although no statistically significant trends through time were found for lakes, this conclusion must be treated with caution. On one hand, the variation in chemistry caused by greatly differing sampling and analytical methodologies is uncertain. On the other hand, all lakes with small areas consistently showed lowered pH's and

conductivities. As well, 84 percent of the lakes in this study displayed some small decrease in alkalinity over time.

Historical stream records had fewer analytical and sampling methodological problems. It is therefore felt that the trends observed in the streams are likely a result of atmospheric deposition and are not an artifact. A significant decrease over time in spring alkalinity and conductivity is evident. Streams consistently exhibited lower pH's, alkalinities, and conductivities in spring and fall in the areas of higher sulphate deposition, although differences were not statistically significant. The evidence of recent bicarbonate alkalinity depletion (by comparison with expected equilibrium levels) in some streams also indicates preliminary stages of acidification.

ACKNOWLEDGEMENTS

The authors thank the Ontario Ministry of Natural Resources, Ontario Ministry of the Environment, the Sea Lamprey Control Centre, and M.G. Johnson for the chemical data analyzed in this report. M.F. Bernier and P. Purych of the OMNR District Offices of Sault Ste. Marie and Blind River were particularly helpful in supplying survey data. Thanks go to W. Keller, OMNR, for his constructive review of

the draft and helpful suggestions, and to H.F. Nicholson for his help in preparing this paper for publication. Our thanks are also extended to W. Cameron, J. Lipsit, M.A. Miltenberg, B. Collins, M. Wieja, and J. Ross, who assisted in data compilation, computer analysis, graphics, and typing.

REFERENCES

ARMSTRONG, D., & SIMPSON, E. 1982. (OMNR at Sault Ste. Marie and Blind River. Personal conversation.)

BARRIE, L.A., & SIROIS, A. 1982. "An analysis and assessment of precipitation chemistry measurements made by CANSAP (The Canadian Network for Sampling Precipitation): 1977-1980". Can. Dept. Environm., Atmos. Environm. Serv., Rept., AQRB-82-003-T., 163 pp.

BEAMISH, R.J., & HARVEY, H.H. 1972. "Acidification of the La Cloche Mountain lakes, Ontario, and resulting fish mortalities". J. Fish. Res. Bd. Can., 29: 1131-1143.

BURNS, D.A., GALLOWAY, J.N., & HENDRY, G.R. 1981. "Acidification of surface waters in two areas of the eastern United States". Wat. Air Soil Pollut., 16: 277-285.

CANADA DEPT. OF THE ENVIRONMENT. 1982. "Canadian climate normals, 1951-1980. Temperature and precipitation, Ontario. Part 4". Atmos. Environm. Ser., 254 pp.

COWLING, D.J., & SCOTT, M. 1975. "Limnological data report for the Marine Department of Environmental Protection". U.S. Geol. Surv., Coop. Lake Stud. Proj., Open-file Rept., 135 pp.

DILLON, P.J., JEFFRIES, D.S., SNYDER, W., REID, R., YAN, N.D., EVANS, D., MOSS, J., & SCHEIDER, W. 1978. "Acidic precipitation in south-central Ontario: recent observations". J. Fish. Res. Bd. Can., 35: 809-815.

GOODCHILD, G. 1982. (OMNR, Fish. Br., Toronto. Personal conversation.)

HAINES, T.A. 1982. "Interpretation of aquatic pH trends". Trans. Amer. Fish. Soc., 111: 779-786.

HENRICKSEN, A. 1979. "A simple approach for identifying and measuring acidification of freshwater". Nature, 278: 542-545.

HENRICKSEN, A. 1980. "Acidification of freshwaters - a large scale titration". In: D. Drabløs & A. Tollan (eds.), 'Proc. Internat. Conf. Ecol. Implact Acid Precip.': 68-74. SNSF-Project, Sandefjord, Norway, 1980.

HENRICKSEN, A. 1982. "Susceptibility of surface waters to acidification". In: T.A. Haines & R.E. Johnson (eds.), 'Acid Rain/Fisheries. Proc. Internat. Symp. Acid Precip. Fish. Impacts North America': 103-121. Amer. Fish. Soc., N.E. Div., 357 pp.

HOWELLS, G. 1982. "Interpretation of aquatic pH trends". Trans. Amer. Fish Soc., 111: 779-786.

JEFFRIES, D.S., & ZIMMERMAN, A.P. 1980. "Comments on the analysis and sampling of low conductivity natural waters for alkalinity". Can. J. Fish. Aquat. Sci., 37: 901-902.

KELLER, W., & GALE, P. 1982. "Monitoring of Lake Superior tributaries, 1980-1981". OME, APIOS Rept., API 009/82, 30 pp.

KELSO, J.R.M., LOVE, R., LIPSIT, J., & DERMOTT, R. 1982. "Chemical and biological status of headwater lakes in the Sault Ste. Marie District, Ontario". In: F.M.D'Itri (ed.), 'Acid Precipitation - Effects of Ecological Systems': 665-207. Ann Arbor Sci. Publ., Michigan.

KRAMER, J.R. & TESSIER, A. 1981. "Acidification of aquatic systems: a critique of chemical approaches". McMaster Univ., Techn. Rept. 30 pp.

LUCAS, A.E., & COWELL, D.W. 1982. "Regional assessment of sensitivity to acid deposition for eastern Canada". Can. Dept. Environm., Lands Direct., Burlington, Ont., Internal Rept.

MINNS, C.D. 1981. "Acid rain: a preliminary estimate of the risk to Ontario's inland fisheries". Can. MS Rept. Fish. Aquat. Sci., (1622).

ONTARIO MINISTRY OF THE ENVIRONMENT. 1980. "Water quality data. Ontario lakes and streams". Wat. Resourc. Br., Toronto, 670 pp.

ONTARIO MINISTRY OF THE ENVIRONMENT. 1981. "1979 water quality summary. Northeast Region". Wat. Resourc. Assessm. Unit, Sudbury.

ONTARIO MINISTRY OF NATURAL RESOURCES. 1980. "An order-based watershed mapping technique". Land Use Coord. Br., Toronto, Internal Rept. 59 pp.

RAWLINGS, M. 1982. (OME, Lab. Serv. Br., Rexdale. Personal conversation.)

SHILTS, W.W. 1981. "Sensitivity of bedrock to acid precipitation: modification by glacial processes". Geol. Surv. Can., Cat. No. M44-81/14E.

THOMPSON, M., ELDER, F.C., DAVIS, A.R., & WHITLOW, S. 1980. "Evidence of acidification of rivers of eastern Canada". In: D. Drabløs & A. Tollan (eds.), 'Proc. Internat. Conf. Ecol. Impact Acid Precip.', SNSF-Project, Sandefjord, Norway, 1980.

WATT, W.D., SCOTT, D., & RAY, S. 1979. "Acidification and other chemical changes in Halifax County lakes after 21 years". Limnol. Oceanogr., 24(6): 1154-1161.

WILLIAMS, M. 1982. (OMNR, Land Use Coord. Br., Toronto. Personal conversation.)

LIST OF TABLES

Table 1 Analytical methods used by data sources from 1959 to 1981 for lake and stream chemistry. Time spans indicate either a change in instrument or method.

Table 2 Percent of chemical measurements made using each sampling method through time in lakes in Sault Ste. Marie and Blind River Districts.

Table 3 Correlation coefficients (r) between mean annual change in chemical parameters and morphological and geological factors. Significance at $P < 0.05$ indicated by *. Each lake's watershed was classified (geological index) according to its sensitivity of bedrock and derived soils to acid loading (based on Shilts, 1981). Data are for lakes in Sault Ste. Marie and Blind River Districts.

Table 4 Summary of statistics for positive and negative mean annual changes in chemical parameters for Sault Ste. Marie and Blind River lakes. Number of lakes are indicated in parenthesis. Standard deviation of the mean (±) follows each mean.

TABLE 1: Analytical Methods Used by Data Sources from 1959 to 1981 for Lake and Stream Chemistry. Time Spans Indicate Either a Change in Instrument or Method.

Data Source	Data	Chronology	Method
STREAM			
Dept. of Fisheries & Oceans Sea Lamprey Control Centre, Sault Ste. Marie	pH	1960-1966	meter; potentiometric
		1976-1978	meter; potentiometric
		1979-1981	meter; potentiometric
	conductivity	1959-1973	meter
		1973-1979	meter
		1979-1981	meter
Dept. of Fisheries & Oceans Great Lakes Fisheries Research Branch, Sault Ste. Marie and Owen Sound	pH	1979-1981	meter; potentiometric
	conductivity	1980-1981	meter
		1979-1981 (SSM)	meter
	alkalinity	1979-1981	meter, total inflection point titrations
	cations/ anions		atomic absorption or emission spectrophotometry
Ministry of the Environment, Sudbury Lab.	pH	1979-1981	meter; potentiometric
	conductivity	1979-1981	meter
	alkalinity	1979-1981	meter; total inflection point titration
Rexdale Lab.	pH	1966-1974	meter; potentiometric
		1975-1981	meter; potentiometric
	conductivity	1966-1974	meter
		1975-1981	meter

(Cont'd...)

TABLE 1: (Cont'd). Analytical Methods Used by Data Sources from 1959 to 1981 for Lake and Stream Chemistry. Time Spans indicate Either a Change in Instrument or Method.

Data Source	Data	Chronology	Method
Rexdale Lab.	alkalinity	1965-1974	meter, total fixed endpoint (TFE) titration
		1975-1981	meter, TFE and total inflection point titrations
	calcium	1966-1974	EDTA Titrimetric
		1975-1981	atomic absorption
	magnesium	1966-1974	EDTA Titrimetric
		1975-1981	atomic absorption
	sulphate	1966-1973	Turbidometric, Hach Sulfaver
		1974-1981	autoanalyzer, MTB method
LAKE DATA			
Ministry of Natural Resources, Sault Ste. Marie and Blind River	pH	1960-1980	Hach, colorimetric, Hellige comparator
		1980-1981	meter, potentiometric
	conductivity	1960-1970	meter
		1971-1981	meter
	alkalinity	1960-1981	Hach, colorimetric, methyl-orange indicator
		1980-1981	meter; total inflection point titration

TABLE 2: Percent of Chemical Measurements Made Using Each Sampling Method Through Time in Lakes in Sault Ste. Marie and Blind River Districts.

Sample Type	1960-1965				1966-1970				1971-1975				1976-1981				% of Total Measurements Made for Each Sample Type			
	Cond	H^+	TFE	TIP	Cond	H^+	TFE	TIP	Cond	H^+	TFE	TIP	Cond	H^+	TFE	TIP	Cond	H^+	TFE	TIP
Surface Grab		100	100		25	74	72		4	16	17		1	1	6		2	25	26	
Integrated (discrete layers in stratum)					75	26	28		96	84	83	100	55	49	92	3	63	49	73	4
Tube Composite													44	49	2	97	35	26	1	96

COND Conductivity
H^+ Hydrogen Ion (pH)
TFE Total Fixed Endpoint Alkalinity
TIP Total Inflection Point Alkalinity

TABLE 3: Correlation Coefficients (r) Between Mean Annual Change in Chemical Parameters and Morphological and Geological Factors. Significance at $P < 0.05$ Indicated by *. Each Lake's Watershed was Classified (Geological Index) According to its Sensitivity of Bedrock and Derived Soils to Acid Loading (Based on Shilts, 1981). Data are for Lakes in Sault Ste. Marie and Blind River Districts.

	Lake Area	Watershed Area	Mean Depth	Lake Order	Geological Index	Latitude	Longitude
Hydrogen	0.082	0.078	0.068	0.016	0.145	0.023	-0.031
Alkalinity	-0.010	0.022	0.008	-0.155	0.113	-0.350*	0.344*
Conductivity	0.129	-0.133	-0.029	0.196	0.059	-0.272*	0.282*
Lake Order	0.340*	0.535*	0.178*		0.272*	0.054	-0.073

TABLE 4: Summary of Statistics for Positive and Negative Mean Annual Changes in Chemical Parameters for Sault Ste. Marie and Blind River Lakes. Number of Lakes are Indicated in Parenthesis. Standard Deviation of the Mean (±) Follows Each Mean.

	Lake Area km^2	Watershed Area km^2	Mean Depth m	Lake Order	Geological Index*
Conductivity					
Negative Change	1.2±1.4(26)	47.5±129.6(24)	9.4±7.1(26)	2.0±0.9(24)	14.5±1.7(26)
Positive Change	3.1±5.3(32)	40.2±100.6(28)	10.3±5.4(32)	2.5±1.1(31)	14.8±2.4(32)
Alkalinity					
Negative Change	2.7±4.9(71)	38.4±102.6(66)	10.5±6.8(70)	2.2±0.9(67)	14.9±2.5(71)
Positive Change	0.6±0.5(11)	11.4± 20.8(11)	8.5±7.3(10)	1.8±0.9(11)	15.2±2.2(11)
Hydrogen					
Negative Change	2.7±0.7(54)	27.8± 10.8(52)	10.3±1.0(53)	2.0±0.2(52)	14.9±2.1(53)
Positive Change	1.9±0.4(63)	30.5± 11.4(59)	9.4±0.8(62)	2.2±0.1(61)	14.9±2.7(63)

* From Shilts (1981).

LIST OF FIGURES

Figure 1 Sensitivity of Ontario lakes and streams to atmospheric deposition based on the spatial distribution of terrain characteristics and precipitation chemistry.

Figure 2 Distribution of streams with recent and historical data, and their alkalinity classes in relation to sulphate deposition.

Figure 3 Mean monthly discharge for typical Lake Superior, North Channel, and Georgian Bay streams from historical records.

Figure 4 Mean annual changes (MAC) in hydrogen-ion, alkalinity, and conductivity in Sault Ste. Marie and Blind River lakes.

Figure 5 Annual change in hydrogen-ion, alkalinity, and conductivity in Sault Ste. Marie and Blind River lakes from 1961 to 1981.

Figure 6 Mean annual change (MAC) in hydrogen-ion and alkalinity concentrations for Sault Ste. Marie and Blind River lakes.

Figure 7 Mean annual changes in hydrogen-ion, alkalinity, and conductivity in spring and fall for Lake Superior, North Channel, and Georgian Bay streams.

Figure 8 Correlation between HCO_3^- and Ca + Mg in the fall for 21 streams and in the spring for 41 streams.

Figure 9 Correlation between SO_4^{2-} and Ca + Mg - HCO_3^- for 21 streams (fall data).

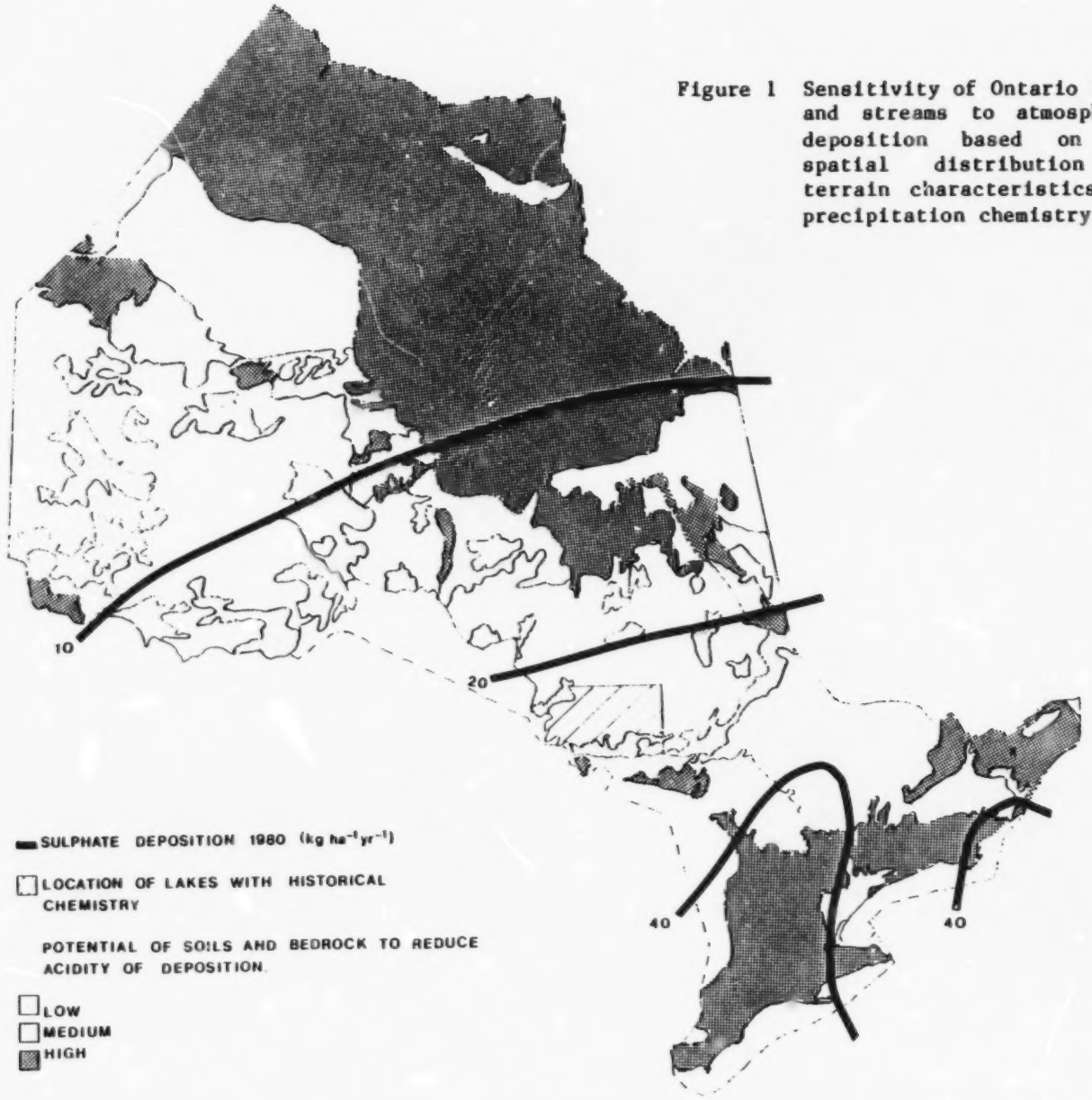

Figure 1 Sensitivity of Ontario lakes and streams to atmospheric deposition based on the spatial distribution of terrain characteristics and precipitation chemistry.

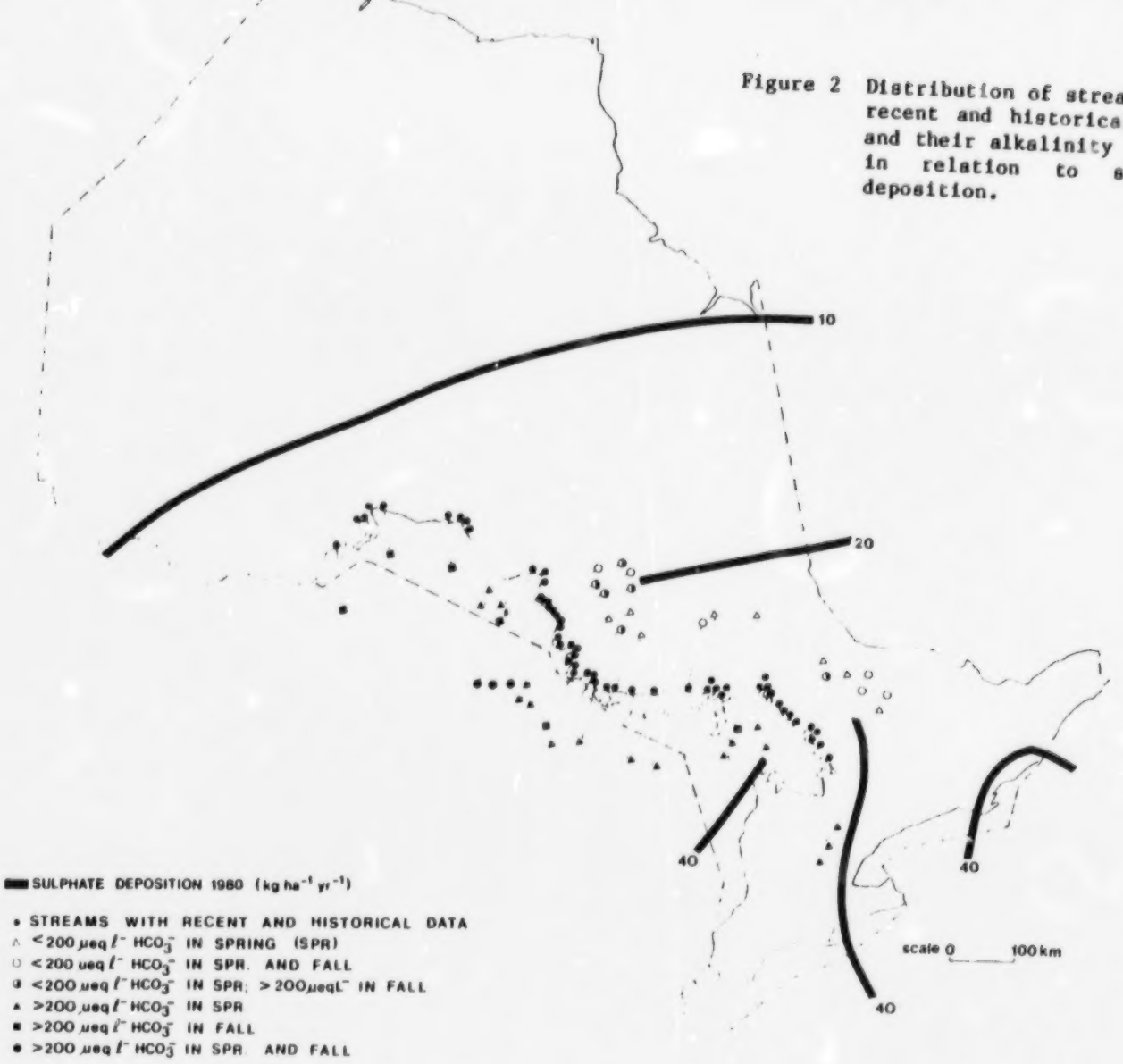
10
20
40
40
40
SULPHATE DEPOSITION 1980 (kg ha⁻¹ yr⁻¹)
• STREAMS WITH RECENT AND HISTORICAL DATA
△ <200 μeq l⁻ HCO3⁻ IN SPRING (SPR)
○ <200 ueq l⁻ HCO3⁻ IN SPR. AND FALL
◑ <200 μeq l⁻ HCO3⁻ IN SPR; >200μeqL⁻ IN FALL
▲ >200 μeq l⁻ HCO3⁻ IN SPR
■ >200 μeq l⁻ HCO3⁻ IN FALL
● >200 μeq l⁻ HCO3⁻ IN SPR. AND FALL
scale 0 100 km

Figure 2 Distribution of streams with recent and historical data, and their alkalinity classes in relation to sulphate deposition.

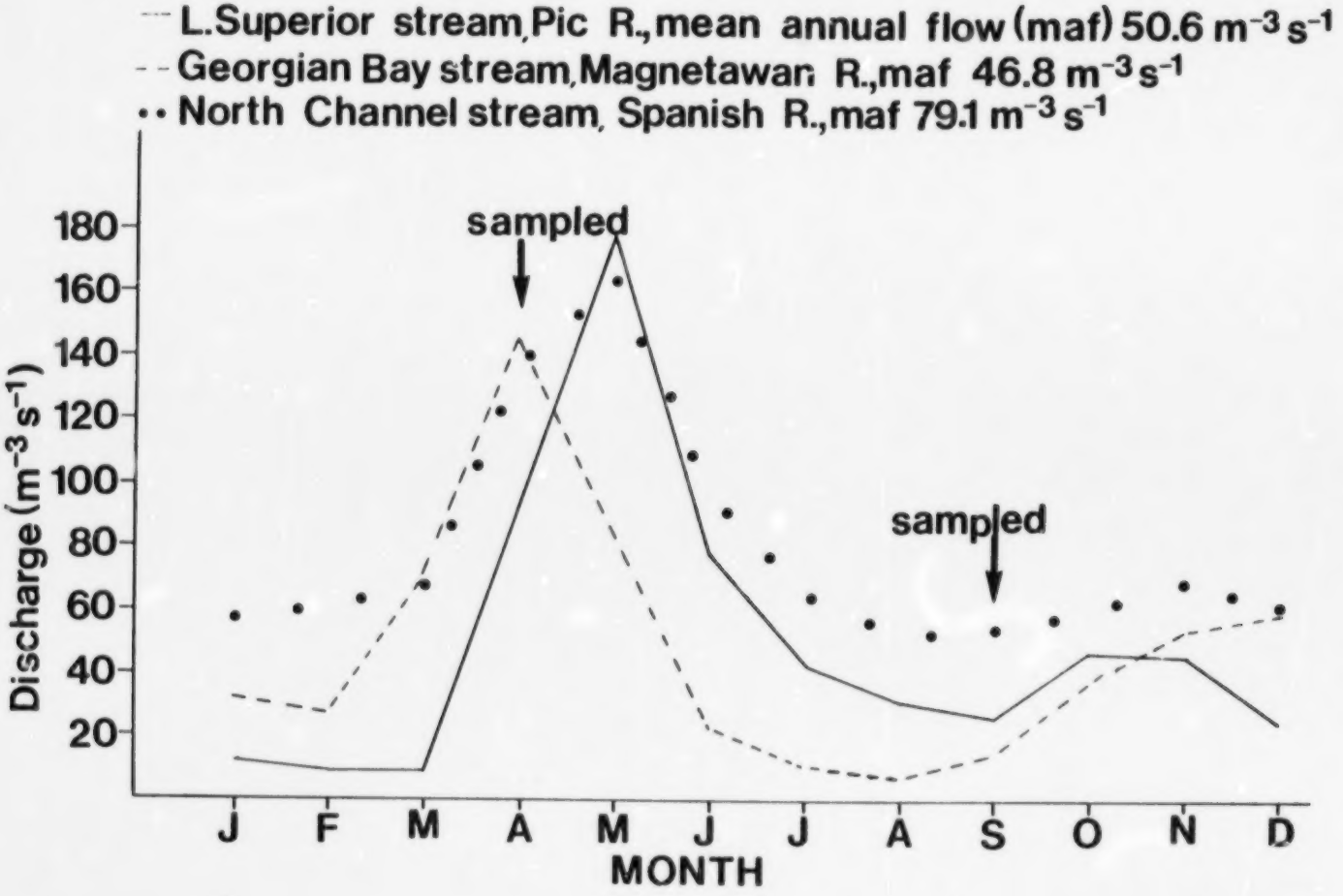

Figure 3 Mean monthly discharge for typical Lake Superior, North Channel, and Georgian Bay streams from historical records.

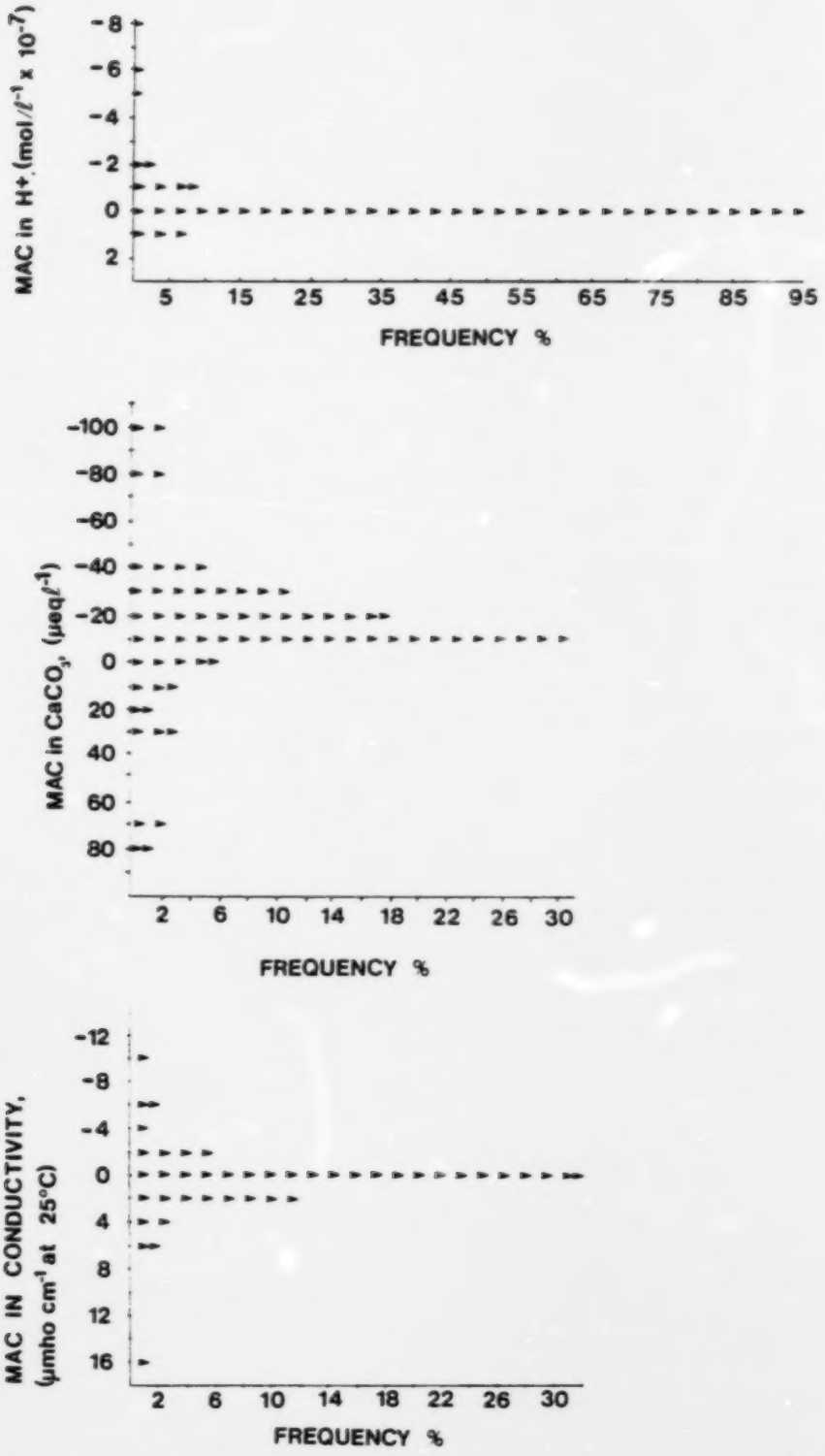

Figure 4 Mean annual changes (MAC) in hydrogen-ion, alkalinity, and conductivity in Sault Ste. Marie and Blind River lakes.

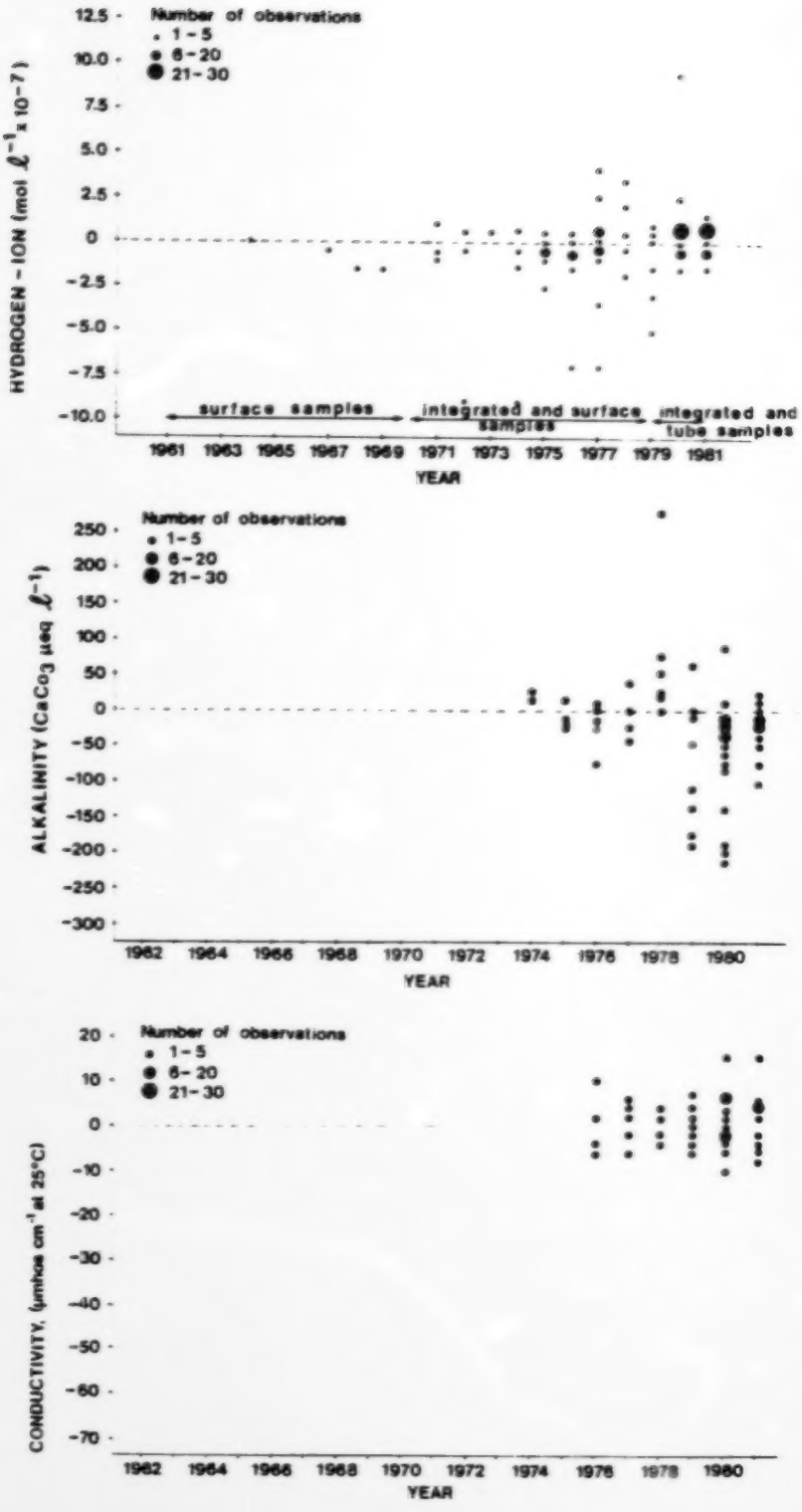

Figure 5 Annual change in hydrogen-ion, alkalinity, and conductivity in Sault Ste. Marie and Blind River lakes from 1961 to 1981.

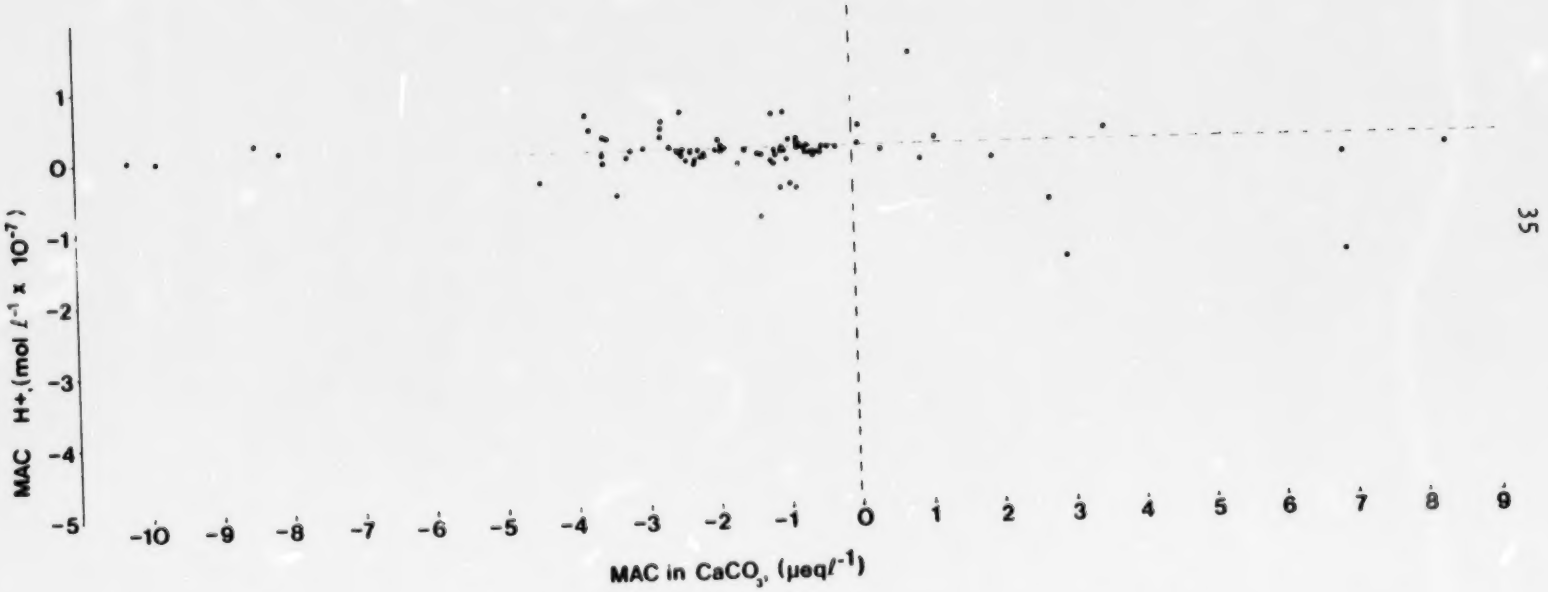

Figure 6 Mean annual change (MAC) in hydrogen-ion and alkalinity concentrations for Sault Ste. Marie and Blind River lakes.

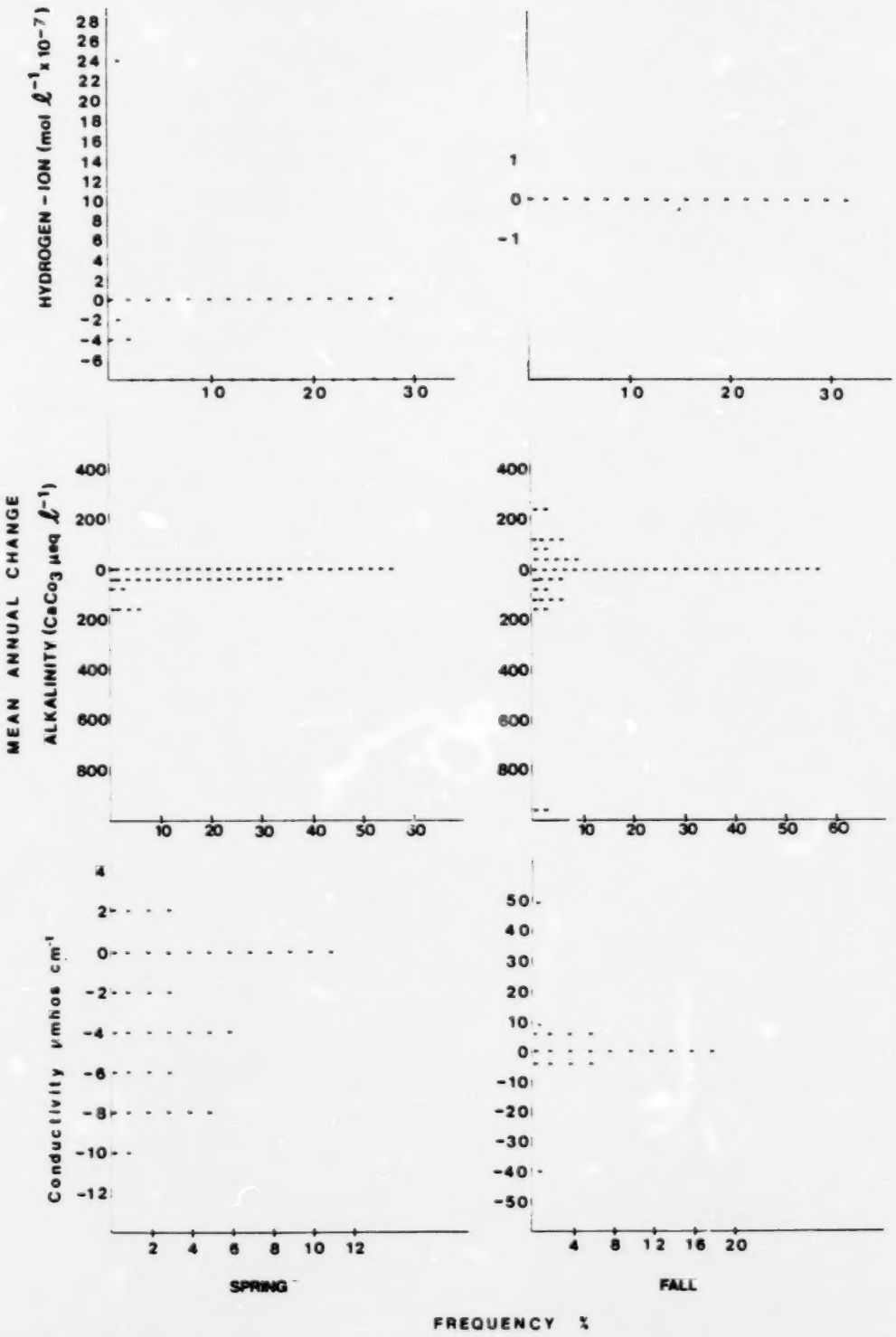

Figure 7 Mean annual changes in hydrogen-ion, alkalinity, and conductivity in spring and fall for Lake Superior, North Channel, and Georgian Bay streams.

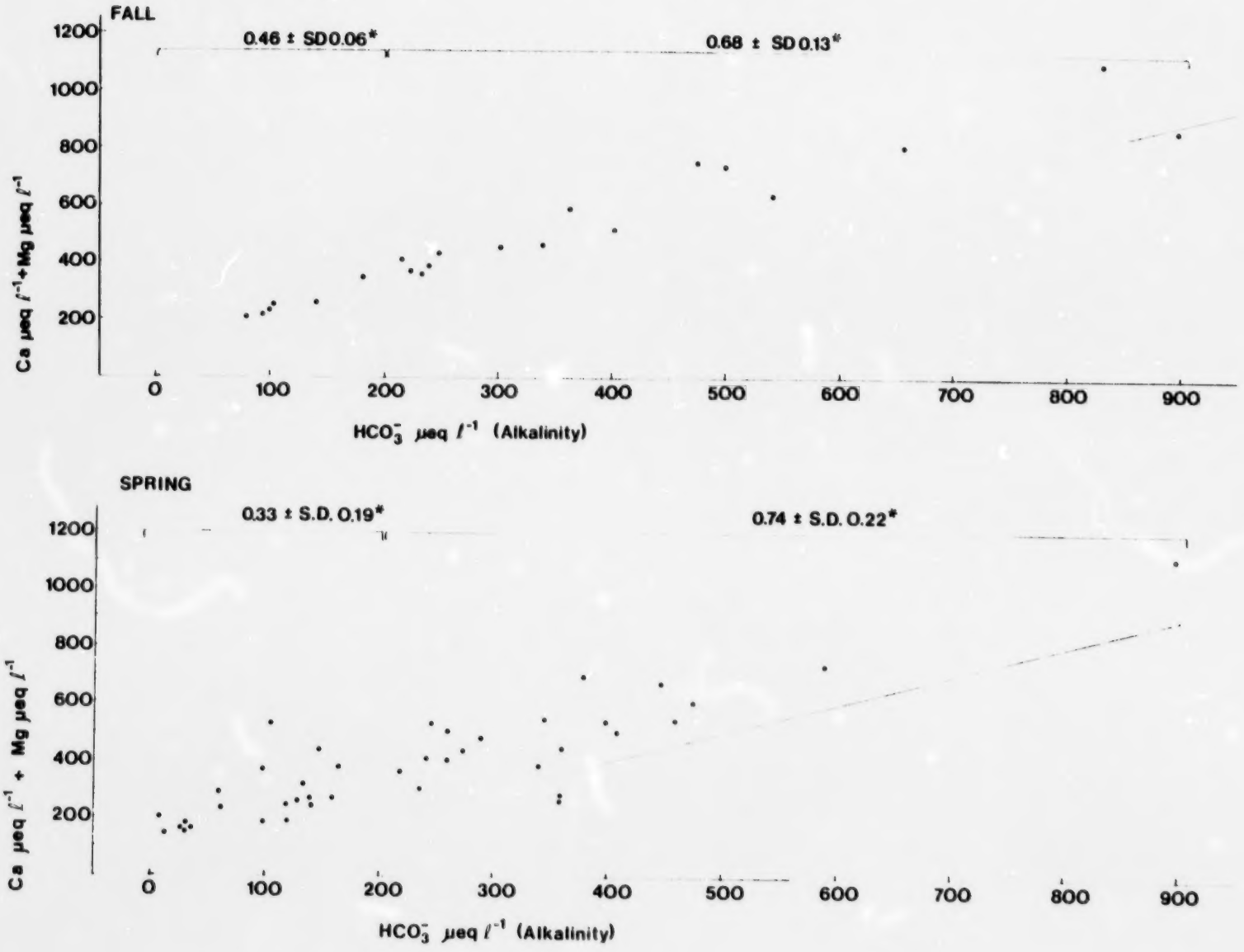
FALL
0.46 ± SD 0.06*
0.68 ± SD 0.13*
Ca μeq ℓ⁻¹ + Mg μeq ℓ⁻¹
HCO₃⁻ μeq ℓ⁻¹ (Alkalinity)
SPRING
0.33 ± S.D. 0.19*
0.74 ± S.D. 0.22*
Ca μeq ℓ⁻¹ + Mg μeq ℓ⁻¹
HCO₃⁻ μeq ℓ⁻¹ (Alkalinity)

Figure 8 Correlation between HCO_3^- and Ca + Mg in the fall for 21 streams and in the spring for 41 streams.

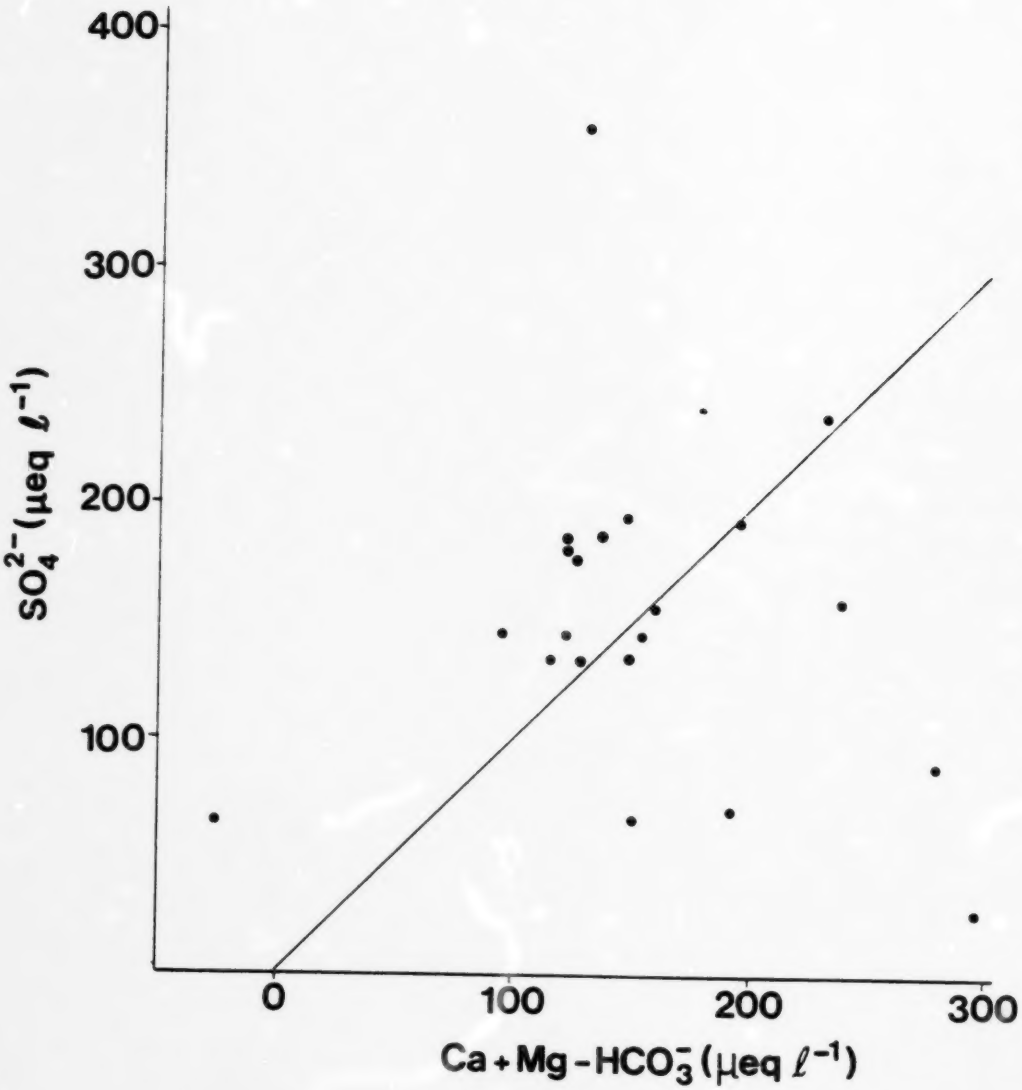

Figure 9 Correlation between SO_4^{2-} and Ca + Mg - HCO_3^- for 21 streams (fall data).